

**ISOTOPIC MEASUREMENTS IN CAIs WITH THE NANOSIMS: IMPLICATIONS TO THE UNDERSTANDING OF THE FORMATION PROCESS OF Ca, Al-RICH INCLUSIONS.** M. Ito and S. Messenger, Robert M. Walker Laboratory for Space Science, ARES, NASA JSC, 2101 NASA Parkway, Houston TX 77573, USA. (motoo.ito-1@nasa.gov, scott.r.messenger@nasa.gov).

**Introduction:** Ca, Al-rich Inclusions (CAIs) preserve evidence of thermal events that they experienced during their formation in the early solar system [e.g. 1]. Most CAIs from CV and CO chondrites are characterized by large variations in O-isotopic compositions of primary minerals, with spinel, hibonite, and pyroxene being more  $^{16}\text{O}$ -rich than melilite and anorthite, with  $\delta^{17,18}\text{O} = \sim -40\%$  ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O} = \sim -20\%$ ) [e.g. 1]. These anomalous compositions cannot be accounted for by standard mass dependent fractionation and diffusive process of those minerals [2]. It requires the presence of an anomalous oxygen reservoir of nucleosynthetic origin or mass independent fractionations before the formation of CAIs in the early solar system [e.g. 3, 4].

The CAMECA NanoSIMS is a new generation ion microprobe that offers high sensitivity isotopic measurements with sub 100 nm spatial resolution. The NanoSIMS has significantly improved abilities in the study of presolar grains in various kind of meteorites [e.g. 5] and the decay products of extinct nuclides in ancient solar system matter [e.g. 6]. This instrument promises significant improvements over other conventional ion probes in the precision isotopic characterization of sub-micron scales.

We report the results of our first O isotopic measurements of various CAI minerals from EK1-6-3 and 7R19-1(a) utilizing the JSC NanoSIMS 50L ion microprobe. We evaluate the measurement conditions, the instrumental mass fractionation factor (IMF) for O isotopic measurement and the accuracy of the isotopic ratio through the analysis of a San Carlos olivine standard and CAI sample of 7R19-1(a).

**Experimental:** We used two CAI samples of 7R19-1(a) and EK1-6-3 from Allende CV meteorite for this study. The polished section of EK1-6-3 was studied by optical microscopy, and BSE imaging and X-ray elemental mapping by CAMECA SX-50 EPMA at the JSC prior to ion probe measurements. Carbon thin film was coated on the surface prior to EPMA and ion probe analysis.

Oxygen isotopic measurements of CAI minerals were performed by in-situ analysis in multi-collection mode using the JSC NanoSIMS 50L. An 8 keV Cs<sup>+</sup> primary ion beam with a diameter of  $\sim 100$  nm was used. The primary beam current was  $\sim 1.3$  pA. The primary beam was rastered over  $5 \times 5$   $\mu\text{m}$  areas for these measurements. Negative secondary ions of  $^{16}\text{O}$ ,  $^{17}\text{O}$

$^{18}\text{O}$ ,  $^{26}\text{Mg}$ ,  $^{27}\text{Al}$ , and  $^{28}\text{Si}$  were measured by EM detectors in multidetection at a high mass resolution of  $M/\Delta M = \sim 9500$  that is sufficient to separate interfering  $^{16}\text{OH}$  to  $^{17}\text{O}$ . The interference was always negligible (typically  $< 0.1$  ‰) in the  $\delta^{17}\text{O}$  notation. A normal-incident electron gun was utilized for charge compensation of the analysis area. Each measurement consisted of 50 cycles of with 20s counting time, lasting 18 minutes. We monitored the Mg/Si and Al/Si ratios during the measurement to check instability of secondary ion intensities due to mineral phases. Each run was started after stabilization of the secondary ion beam following pre-sputtering procedure. During the isotopic analysis, the mass peaks were centered automatically after every 10 cycles. Terrestrial San Carlos olivine standard (Fo90) was used to correct the IMF. The typical precision on  $\Delta^{17}\text{O}$  is  $\sim 3$  ‰ ( $1\sigma$ ) on each measurement; the reproducibility is  $\sim 2$  ‰ ( $1\sigma$ ).

We also acquired a two-dimensional isotopic map of the boundary between melilite and spinel in 7R19-1(a) by the JSC NanoSIMS. Basic measured conditions were same that we described in the previous section. The measured area was  $25 \times 25$   $\mu\text{m}$  by rastering. A normal incident electron gun was applied prevent charging of the rastered area.

**Results and Discussion:** In briefly, 7R19-1(a) is a fassaite-rich, compact Type-A CAI. 7R19-1 consists mainly of melilite, fassaite and spinel grains. Hibonites, perovskites and anorthites occur in the CAI as minor minerals. The detailed petrographic texture, chemical compositions, and isotopic distributions of O, Mg and K in 7R19-1(a) were published in [7-9].

EK1-6-3 is a rectangle shaped CAI with  $\sim 400 \times 500$   $\mu\text{m}$  in size. Half of the CAI is surrounded by layered rim structures. EK1-6-3 mainly consists of melilite, anorthite and pyroxene. Average of åkermanite composition of core melilite is close to Ak20, which is similar to that of Type A CAI [10]. The pyroxenes in the core are large ( $200 \times 100$   $\mu\text{m}$ ) euhedral Ti-rich fassaite crystals containing strong concentric zoning. The core fassaite have Ti-rich ( $\text{TiO}_2$ : 9-12 wt%). Anorthite is nearly An99, and shows as an euhedral lath. The CAI rim region consists of different mineral aggregates: irregularly shaped Fe-rich spinel, small rounded perovskite, Fe-rich forsterite, melilite, anorthite and pyroxene. All spinels indicate an anhedral texture near the CAI rim. Those spinels are Fe-rich composition of

Mg/(Mg+Fe) ~60-80 %. There are small amounts of perovskite grains in the melilite and alteration in the rim. The rim melilites show  $\sim \text{\AA}8$ . Pyroxenes in the rim have different chemical compositions with those in the core. The pyroxenes in the rim show low  $\text{TiO}_2$  ~0.04 %, relatively low CaO ~12 % and high  $\text{Na}_2\text{O}$  ~2.5 % that is in contrast with core fassaite.

Our first O isotopic measurements of CAI 7R19-1(a) were obtained from locations previously measured and described in [7, 8]. Major refractory minerals (spinel, fassaite and melilite) in 7R19-1(a) showed large negative anomalies of  $\Delta^{17}\text{O}$  in the order, spinel ( $\sim -30 \pm 3$  ‰ (1 $\sigma$ ))  $\sim$   $^{16}\text{O}$ -rich melilite ( $\sim -30 \pm 4$  ‰)  $>$   $^{16}\text{O}$ -poor melilite ( $\sim -17 \pm 4$  ‰)  $\sim$  fassaite ( $\sim -11 \pm 7$  ‰). The  $\Delta^{17}\text{O}$  for each of these mineral are slightly, and systematically  $^{16}\text{O}$ -enriched ( $\sim 10$  ‰) compared with the previously published analyses. This enrichment may be due to the  $^{16}\text{O}$  beam irradiation during the Mg and K isotopic measurements in [9]. If we take into account of the  $^{16}\text{O}$ -enrichment difference between this study and previous works [7, 8], the O isotopic compositions and  $\Delta^{17}\text{O}$  are in good agreement with the previous measurements.

O isotopic ratios of melilite, anorthite, and fassaite in the EK1-6-3 CAI fall on the CCAM line (Fig 1). Core pyroxenes show  $^{16}\text{O}$  enrichment ( $\Delta^{17}\text{O} = -17 \pm 3$  ‰), while melilite and anorthite show  $^{16}\text{O}$ -poor compositions ( $\Delta^{17}\text{O}$  in melilite =  $-7 \pm 6$  ‰,  $\Delta^{17}\text{O}$  in anorthite =  $-3 \pm 4$  ‰). The results for those minerals show same O isotopic characteristics as most of the CAIs [e.g. 1]. Melilite, pyroxene, and anorthite in the core are isotopically homogeneous within 3-6 ‰. Our results indicate that the CAI formed initially in a  $^{16}\text{O}$ -rich region similar to most refractory objects [e.g. 1, 7, 8].

Figure 2 is an isotopic image of  $^{28}\text{Si}/^{27}\text{Al}$  of the crystal boundary between  $^{16}\text{O}$ -rich melilite and  $^{16}\text{O}$ -rich spinel in 7R19-1(a). The O isotopic compositions of the melilite and spinel grains determined from this image are the same within error, and agree with values we determined by spot analysis of these minerals. The O isotopic composition of the field of view ( $25 \times 25$   $\mu\text{m}$ ) of this image was found to be  $\Delta^{17}\text{O} = -36 \pm 4$  ‰ (1 $\sigma$ ). Here we were able to show that the spinel inclusions had a  $\Delta^{17}\text{O}$  of  $-30 \pm 6$  ‰, matching the values we determined in the spinel grain by spot analysis. A  $\Delta^{17}\text{O}$  of melilite from the image was  $-39 \pm 5$  ‰, which is good agreement with the value by spot analysis within a error.

The arrows in the figure indicate the positions of tiny (0.7 - 2.0  $\mu\text{m}$ ) spinel grains scattered within the  $^{16}\text{O}$ -rich melilite crystal. There have been previous reports of numerous tiny spinel grains the  $^{16}\text{O}$ -rich melilite, but it has not been possible to determine their

O isotopic compositions due to instrumental limitations. These small spinel grains gave insufficient signal to accurately determine their individual O isotopic ratios in this image. However, in future isotopic imaging studies, the measurement conditions can be optimized to better determine the O isotopic compositions of at  $\mu\text{m}$  spatial scales.

**References:** [1] Clayton R.N. et al. (1997) *EPSL*, **34**, 209-224. [2] Ryerson F.J. and McKeegan K.D. (1994) *GCA*, **58**, 3713-3734. [3] Yurimoto H. and Kuramoto K. (2002) *Science*, **305**, 1763-1766. [4] Young E. and Lyon I. (2005) *Nature*, **435**, 317-320. [5] Nittler L.R. (2003) *EPSL*, **209**, 259-273. [6] Mostefaoui S. et al. (2005) *ApJ*, **625**, 271-277. [7] Yurimoto H. et al. (1998) *Science*, **282**, 1874-1877. [8] Ito M. et al. (2004) *GCA*, **68**, 2905-2923 [9] Ito M. et al. (2006) *Meteoritics & Planet. Sci.*, **41**, 1871-1882. [10] Grossman et al. (1975) *GCA*, **39**, 433-454.

